

1 IAP20 Rec'd PCT/PTO 26 JAN 2006

DESCRIPTION

STABILIZING AGENT FOR HYDROALKOXYASILANE, STABILIZATION METHOD,
AND STABILIZED HYDROALKOXYASILANE

5

Technical Field

[0001] The present invention relates to a stabilizing agent for a hydroalkoxysilane during storage or transportation thereof, as well as to a method for stabilizing a hydroalkoxysilane and to a hydroalkoxysilane stabilized with the aforementioned stabilizing agent.

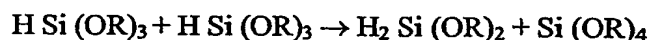
10

Background Art

[0002] Hydroalkoxysilanes are industrially important compounds as intermediates used in manufacturing various organosilicon compounds and silicon-functional polymers. Since they contain at least one silicon-bonded hydrogen atoms as well as at least one silicon-bonded alkoxy groups in the molecule, they possess high reactivity and require a great deal of attention during storage and transportation. Normally, hydroalkoxysilanes are highly volatile and should be kept in sealed containers. The problem associated with their storage is that under the effect of the reaction described below, a hydroalkoxysilane either loose purity, undergo chemical changes, or develop an increased pressure in a storage container.

20

- 1) A dihydroalkoxysilane represented by the general formula: $\text{H}_2\text{Si}(\text{OR})_2$ wherein R is alkyl group that is a low-boiling-point compound resulting from a disproportionation reaction is formed in accordance with the following scheme:



25

- 2) Gaseous hydrogen is generated under the effect of a dehydration reaction with participation of hydrochloric acid, an alcohol, or moisture.

[0003] Various attempts have been made to solve the above problems. For example, Japanese Unexamined Patent Application Publication (hereinafter referred to as Kokai) S55-72198 discloses a method based on coexistence of a hydroalkoxysilane with an organophosphorous compound, while Kokai S63-313790 is based on the use of an organic halide. Kokai H1-90192 exemplifies methods where a hydroalkoxysilane is combined with an inorganic acid or a Lewis acid. However, all these methods still could not provide sufficient stability to the hydroalkoxysilane.

It was proposed in Kokai H6-220417 to use an epoxide, and in Kokai H10-72209 it was reported that admixing a hydroalkoxysilane with a hydrocarbon optionally having a functional group selected from the group consisting of among carboxylic ester, aldehyde, keto, ether, thioether, tertiary amino, epoxy and cyano groups and halogen atoms is effective for stabilization. Furthermore, Kokai H9-77779 discloses a purification method for a

30

35

BEST AVAILABLE COPY

hydroalkoxysilane by admixing it with methyl formate. However, since these organic compounds are soluble in hydroalkoxysilanes, the aforementioned method requires subsequent removal operations.

5

Summary of the Invention

[0004] As a result of extensive studies aimed at finding an improved stabilizing agent for a hydroalkoxysilane, a improved stabilization method, and a stabilized hydroalkoxysilane which are free of the aforementioned drawbacks, the inventors have revealed that a hydroalkoxysilane can be efficiently stabilized with a carboxylate, and that coexistence of a hydroalkoxysilane with a carboxylate can eliminate such problems as loss of purity and chemical changes during storage and transportation, and a pressure rise in a storage container. Such coexistence provides a stabilized hydroalkoxysilane and facilitates separation and removal of the stabilizing agent from the stabilized hydroalkoxysilane after storage and transportation. Thus the inventors arrived at the present invention. In view of the above, it is an object of the present invention to provide an improved stabilizing agent and an improved method that stabilizes a hydroalkoxysilane, provide a hydroalkoxysilane with improved stability, and facilitate separation and removal of the stabilizing agent after storage and transportation of the stabilized hydroalkoxysilane are completed.

20

[0005] Namely, the present invention relates to the following;

- [1] A stabilizing agent for a hydroalkoxysilane characterized by comprising a carboxylate.
- [2] The stabilizing agent according to [1], wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 18 carbon atoms.
- [3] The stabilizing agent according to [2], wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms.
- [4] The stabilizing agent according to [3], wherein said alkali metal salt or alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms are selected from the group consisting of sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate or pentanoate, sodium oxalate, potassium formate, potassium acetate, magnesium acetate, and calcium acetate.
- [5] A method for stabilizing a hydroalkoxysilane characterized by the fact that said hydroalkoxysilane coexists with a carboxylate.
- [6]. The method according to [5], wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 18 carbon atoms.
- [7] The method according to [6], wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms.
- [8] The method according to [7], wherein said alkali metal salt or alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms are selected from the group consisting of sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate or pentanoate,

sodium oxalate, potassium formate, potassium acetate, magnesium acetate, and calcium acetate.

5 [9] The method according to [5], wherein said carboxylate coexists with said hydroalkoxysilane in an amount of 0.0001 to 10 parts by weight per 100 parts by weight of said hydroalkoxysilane.

[10] The method according to [5], wherein said hydroalkoxysilane is a trialkoxysilane.

[11] The method according to [10], wherein said trialkoxysilane is trimethoxysilane or triethoxysilane.

[12] The method according to [5], wherein said hydroalkoxysilane is an alkyltrialkoxysilane.

10 [13] The method according to [12], wherein said alkyltrialkoxysilane is a methyltrimethoxysilane or methyltriethoxysilane.

[14] A hydroalkoxysilane characterized by being stabilized with a carboxylate.

[15] The hydroalkoxysilane according to [14], wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 18 carbon atoms.

15 [16] The hydroalkoxysilane according to [14], wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms

[17]. The hydroalkoxysilane according to [16], wherein said alkali metal salt or alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms are selected from the group consisting of sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate or pentanoate, sodium oxalate, potassium formate, potassium acetate, magnesium acetate, and calcium acetate.

20

[0006] A stabilizing agent of the present invention can protect a hydroalkoxysilane from the loss of purity and chemical changes during storage and transportation, prevent a pressure rise in a container where the hydroalkoxysilane is stored, and facilitate separation of a stabilizing agent from the stabilized hydroalkoxysilane by filtering or centrifugation when the hydroalkoxysilane is used as a reactant, a reaction starting material, or an additive and when it is required to obtain a product or a composition free of any stabilizing agent residue.

25

[0007] A stabilization method of the present invention can prevent a hydroalkoxysilane from the loss of purity and chemical changes during storage and transportation, prevent a pressure rise in a container where the hydroalkoxysilane is stored, and facilitate separation of a stabilizing agent from the stabilized hydroalkoxysilane by filtering or centrifugation when the hydroalkoxysilane is used as a reactant, a reaction starting material, or an additive and when it is required to obtain a product or a composition free of any stabilizing agent residue.

30

35

[0008] A stabilized hydroalkoxysilane of the present invention is not subject to loss of purity and chemical changes during storage and transportation, and a pressure rise in a

container where the hydroalkoxysilane is stored, and facilitate separation of a stabilizing agent from the stabilized hydroalkoxysilane by filtering or centrifugation when the hydroalkoxysilane is used as a reactant, a reaction starting material, or an additive and when it is required to obtain a product or a composition free of any stabilizing agent residue.

5

Best Mode for Carrying Out the Invention

[0009] A carboxylate coexisting with a hydroalkoxysilane protects the hydroalkoxysilane from loss of purity and chemical changes, and prevents a pressure rise in a storage container where the hydroalkoxysilane is stored. Furthermore, since the carboxylate is not soluble in the hydroalkoxysilane, if necessary, it can be easily separated from the hydroalkoxysilane by filtering or centrifugation and thus removed. Thus, one should not be concerned that the carboxylate may remain in, or be admixed with, the hydroalkoxysilane as an impurity.

[0010] The aforementioned carboxylate can be represented by an alkali metal salt or alkali earth metal salt of a carboxylic acid. A preferable carboxylic acid is a monocarboxylic acid, but it can also be represented by a dicarboxylic acid, tricarboxylic acid, or a similar polycarboxylic acid. The aforementioned carboxylic acids may contain 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms, and even more preferably 1 to 5 carbon atoms. If the number of carbon atoms exceeds the upper recommended limit, this will increase the molecular weight, and reduce the share of the carboxylic acid component relative to the addition amount, and therefore will require the use of the carboxylate in a larger quantity. An alkali metal may comprise sodium or potassium, and an alkali earth metal can be represented by magnesium and calcium.

[0011] The following are examples of carboxylic acids suitable for the purposes of the present invention: sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate or sodium pentanoate, sodium oxalate, potassium formate, potassium acetate, magnesium acetate, and calcium acetate. Sodium acetate is most preferable since it is easily obtainable and easy to handle. Regarding the carboxylate, an anhydride is preferable since it does not cause hydrolysis of the hydroalkoxysilane, and the form of powder or granule at room temperature is preferable since it can be easily filtered. There are no special restrictions with regard to the size of the powder or granule, but in general its size may be within the range of 1 to 1000 μm .

[0012] It is recommended for a carboxylate to coexist with a hydroalkoxysilane in an amount of 0.0001 to 10 parts by weight, preferably 0.001 to 5 parts by weight, and even more preferably 0.01 to 3 parts by weight per 100 parts by weight of the hydroalkoxysilane. If the carboxylate is used in an amount less than the lower recommended limit, it may be difficult to provide the hydroalkoxysilane with sufficient stability. If, on the other hand, the

carboxylate is used in an amount exceeding the upper recommended limit, it may impair workability for separating and removing the carboxylate.

[0013] The hydroalkoxysilane has at least one silicon-bonded hydrogen atoms and at least one silicon-bonded alkoxy groups in one molecule. It is preferably represented by the following general formula (1): $H(R^1)_xSi(OR^2)_{3-x}$ (1)

In this formula, R^1 is a univalent hydrocarbon group that is exemplified by methyl group, ethyl group, propyl group, isopropyl group, butyl group, cyclohexyl group, or a similar alkyl group; a vinyl group, allyl group, butenyl group, hexenyl group, or a similar alkenyl group; phenyl group, tolyl group, xylyl group, or a similar aryl group. Of these, most preferable is an alkyl group with 1 to 18 carbon atoms, preferably 1 to 6 carbon atoms; R^2 is an alkyl group with 1 to 5 carbon atoms, and "x" is 0, 1, or 2.

[0014] The following are representative examples of hydroalkoxysilanes suitable for the purposes of the present invention: a hydrotrialkoxysilane (i.e., trialkoxysilane), hydroalkyldialkoxysilane (i.e., alkylalkoxysilane), and hydrodialkylalkoxysilane (i.e., dialkylalkoxysilane). The trialkoxysilane can be represented by trimethoxysilane, triethoxysilane, tri-(n-propoxy) silane, and tri-(iso-propoxy) silane. The alkylalkoxysilane can be represented by methyldimethoxysilane, methyldiethoxysilane, methyldi-(iso-propoxy) silane, ethyldimethoxysilane, ethyldiethoxysilane, n-butyldimethoxysilane, tert-butyldimethoxysilane, and cyclohexyldimethoxysilane. A dialkylalkoxysilane can be represented by dimethylmethoxysilane and dimethylethoxysilane.

[0015] A carboxylate can be combined with the aforementioned hydroalkoxysilane by adding the carboxylate to the hydroalkoxysilane and stirring, mixing, or shaking. The stabilized hydroalkoxysilane in accordance with the present invention can be easily produced by adding the carboxylate to the hydroalkoxysilane and then subjecting them to stirring, mixing, or shaking. In order to prevent vaporization of the hydroalkoxysilane and contact with moisture of air, it is recommended to store the stabilized hydroalkoxysilane in a sealed container. Coexistence of the hydroalkoxysilane with the aforementioned stabilizing agent protects the hydroalkoxysilane from the loss of purity and chemical changes during storage and transportation, and prevents a pressure rise in a storage container. As a result, it becomes possible to prolong the storage time and to provide safety during transportation. When the stabilized hydroalkoxysilane is used as a reagent, a starting material, or as an additive, the stabilizing agent can be easily separated by filtering or centrifugation and then removed, so that the product or composition will be free of any stabilizing agent residue.

Examples

[0016] In the subsequent examples and comparative examples, GC% designates percentage determined from the specific surface area on a gas-chromatography chart.

[0017] Example 1

- 5 A 20 mL glass test tube was filled with a 10 g of triethoxysilane and 0.01 g of powdered anhydrous sodium acetate (a commercially produced special-class reagent). The test tube was sealed and held at 25°C. Thirty days later, purity of triethoxysilane contained in the test tube and the amount of generated tetraethoxysilane were measured by means of gas chromatography. The results of measurements are shown in Table 1. After the test tube with
10 the 30-day stored content was well shaken, the mixture of the aforementioned 10 g of triethoxysilane and 0.01 g of powdered anhydrous sodium acetate was almost instantly filtered through a membrane filter (a polytetrafluoroethylene filter having a 0.45 μ m diameter perforations; the product of Millipore Corporation; trademark "Millex-FH") fit onto the tip of the 20 mL glass syringe. As a result, the entire content of the powdered
15 sodium acetate was filtered out.

[0018] Example 2 and Example 3

- The process was conducted in the same manner as in Example 1, with the exception that powdered anhydrous sodium formate (a commercially produced special-class reagent) and
20 powdered anhydrous potassium acetate (a commercially produced special-class reagent) were used instead of the aforementioned powdered sodium acetate. The results of measurements after the storage are shown in Table 1. Furthermore, after 30-day storage under the same conditions as in Example 1, the product was almost instantly filtered through a membrane filter. As a result, the entire content of the powdered sodium formate and
25 powdered potassium acetate was filtered out.

[0019] Comparative Example 1

- The process was conducted in the same manner as in Example 1, with the exception that liquid methyl formate was used instead of the aforementioned powdered sodium acetate.
30 The product was stored and measured as in Example 1. After storage, however, the methyl formate was found dissolved in triethoxysilane and removal thereof required an additional operation, such as distillation.

[0020] Comparative Example 2

- 35 10 g of triethoxysilane were loaded into a 20 mL glass sample tube without addition of any stabilizing agent, such as the powdered sodium acetate. The test tube was sealed, and the content was stored at 25°C. Thirty days later, purity of the triethoxysilane and a produced amount of the tetraethoxysilane were measured with the use of gas chromatography. The results of measurements are shown in Table 1.

[0021] Table 1

	Stabilizing agent	Triethoxysilane (GC%)	Tetraethoxysilane (GC%)
Example 1	Sodium acetate	99.9	0.1
Example 2	Sodium acetate	99.9	0.1
Example 3	Potassium acetate	99.9	0.1
Comparative Example 1	Methyl formate	99.7	0.2
Comparative Example 2	None	96.3	3.5

[0022] Example 4, Example 5 and Example 6

The process was conducted and the product was stored in the same manner as in Example 1, Example 2 and Example 3, except that methyldimethoxysilane was used instead of triethoxysilane. After 30-day storage, the residual amount of the methyldimethoxysilane and the produced amount of methyltrimethoxysilane contained in the test tube were measured by gas chromatography. The results are shown in Table 2.

[0023] Comparative Example 3

The process was conducted and the product was stored in the same manner as in Example 1, with the exception that liquid methylglycidyl ether was used instead of the powdered sodium acetate. The results are shown in Table 2. After storage, however, the methylglycidyl ether was found dissolved in triethoxysilane and removal thereof required additional operations of filtering and distillation.

[0024] Comparative Example 4

10 g of methyldimethoxysilane were loaded into a 20 mL glass-made sample tube without addition of any stabilizing agent, such as the powdered sodium acetate. The test tube was sealed, and the content was stored at 25°C. Thirty days later, a residual amount of the methyldimethoxysilane and a produced amount of the methyltrimethoxysilane contained in the test tube were measured with the use of gas chromatography. The results of measurements are shown in Table 2.

[0025] Table 2

	Stabilizing agent	Methyldimethoxy-silane (GC%)	Methyltrimethoxy-silane (GC%)
Example 4	Sodium acetate	99.9	0.1
Example 5	Potassium acetate	99.8	0.1
Example 6	Potassium acetate	99.9	0.1
Comparative Example 3	Methylglycidyl ether	99.7	0.1
Comparative Example 4	None	99.3	3.6

[0026] Example 7

A 100 mL glass flask with a drain valve was filled with 20 g of methyltrimethoxysilane and 0.02 g of powdered anhydrous sodium acetate (a commercially produced reagent of a special class). The flask was sealed, and the content heated for 3 days in an oil bath at 50°C. Upon completion of heating, the flask was cooled to room temperature, the drain valve was opened, the amount of the generated gas was measured, and it was confirmed that pressure developed inside the flask. Purity of the methyltrimethoxysilane and the amount of the formed methyltrimethoxysilane were measured by gas chromatography. The results are shown in Table 3. After 3-day heating, a mixture composed of 20 g of methyltrimethoxysilane and 0.02 g of powdered sodium acetate was filtered in the same manner as in Example 1 with almost instant separation of the entire powdered sodium acetate.

[0027] Comparative Example 5

The test was carried out in a methyltrimethoxysilane under the same conditions as in Example 7, with the exception that the powdered sodium acetate was not used. The results are shown in Table 3.

[0028] Table 3

	Stabilizing agent	Amount of generated gas (mL)	Methyltrimethoxysilane (GC%)	Methyltrimethoxysilane (GC%)
Example 7	Sodium acetate	Less than 0.1	99.9	0.1
Comparative Example 5	None	4.8	95.0	4.8

Industrial Applicability

[0029] The stabilizing agent and the stabilization method of the present invention are useful for protecting a hydroalkoxysilane from the loss of purity and chemical changes during storage and transportation, and preventing a pressure rise in a storage container. A stabilized hydroalkoxysilane of the present invention is very useful in various industries since it does not lose its purity, is not subject to chemical changes during transportation and storage, and prevents a pressure rise in a storage container.

CLAIMS

1. A stabilizing agent for a hydroalkoxysilane characterized by comprising a carboxylate.
- 5 2. The stabilizing agent according to claim 1, wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 18 carbon atoms.
3. The stabilizing agent according to claim 2, wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms.
- 10 4. The stabilizing agent according to claim 3, wherein said alkali metal salt or alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms are selected from the group consisting of sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate or pentanoate, sodium oxalate, potassium formate, potassium acetate, magnesium acetate, and calcium acetate.
- 15 5. A method for stabilizing a hydroalkoxysilane characterized by the fact that said hydroalkoxysilane coexists with a carboxylate.
- 20 6. The method according to claim 5, wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 18 carbon atoms.
7. The method according to claim 6, wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms.
- 25 8. The method according to claim 7, wherein said alkali metal salt or alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms are selected from the group consisting of sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate or pentanoate, sodium oxalate, potassium formate, potassium acetate, magnesium acetate, and calcium acetate.
- 30 9. The method according to claim 5, wherein said carboxylate coexists with said hydroalkoxysilane in an amount of 0.0001 to 10 parts by weight per 100 parts by weight of said hydroalkoxysilane.
- 35 10. The method according to claim 5, wherein said hydroalkoxysilane is a trialkoxysilane.
11. The method according to claim 10, wherein said trialkoxysilane is a trimethoxysilane or a triethoxysilane.

12. The method according to claim 5, wherein said hydroalkoxysilane is an alkylaldialkoxysilane.

5 13. The method according to claim 12, wherein said alkylaldialkoxysilane is a methyltrimethoxysilane or a methyltriethoxysilane.

14. A hydroalkoxysilane characterized by being stabilized with a carboxylate.

10 15. The hydroalkoxysilane according to claim 14, wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 18 carbon atoms.

16. The hydroalkoxysilane according to claim 14, wherein said carboxylate is an alkali metal salt or an alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms

15

17. The hydroalkoxysilane according to claim 16, wherein said alkali metal salt or alkali earth metal salt of a carboxylic acid having 1 to 5 carbon atoms are selected from the group consisting of sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium valerate or pentanoate, sodium oxalate, potassium formate, potassium acetate, magnesium acetate, and calcium acetate..

20

25

30

35

INTERNATIONAL SEARCH REPORT

International Application No

JP2004/011322

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K15/04 C07F7/02 C07F7/08 C07F7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 113 751 A (ARNOLD HANFRIED) 12 September 1978 (1978-09-12) claims 1,2	1-4
X	US 2 364 410 A (DONALD WHITTAKER) 5 December 1944 (1944-12-05) example 5	1-4
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 591 (C-1272), 11 November 1994 (1994-11-11) & JP 06 220417 A (SHIN ETSU CHEM CO LTD), 9 August 1994 (1994-08-09) abstract	5-17
	----- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

29 October 2004

Date of mailing of the international search report

09/11/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Wengeler, H

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP2004/011322

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 016, no. 033 (C-0905), 28 January 1992 (1992-01-28) & JP 03 244666 A (KANSAI PAINT CO LTD); 31 October 1991 (1991-10-31) abstract</p> <p>-----</p>	5-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP2004/011322

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 4113751	A	12-09-1978	DE	2546063 A1	21-04-1977
			CA	1064018 A1	09-10-1979
			HU	172301 B	28-07-1978
			NL	7611071 A	13-04-1977
US 2364410	A	05-12-1944	GB	545500 A	29-05-1942
			BE	459043 A	
			FR	910864 A	20-06-1946
JP 06220417	A	09-08-1994	JP	2925875 B2	28-07-1999
JP 03244666	A	31-10-1991	NONE		

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☒ **FADED TEXT OR DRAWING**

☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.